

## SULFUR ENRICHMENT VIA VOLATILE-RICH METASOMATISM IN MONTFERRIER XENOLITHS (SOUTHERN FRANCE): CONSEQUENCES FOR HIGHLY SIDEROPHILE ELEMENTS IN THE SUB-CONTINENTAL MANTLE

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### ABSTRACT

Sulfides are the main hosts for highly siderophile elements (HSE); therefore the mantle S content is a crucial datum for geochemical studies relevant to platinum-group element abundances or Re-Os systematics. The estimated S content of the primitive mantle is about  $250 \pm 50$  ppm. Although S contents of fertile peridotite from orogenic massifs support this estimate, peridotites hosted in alkali basalt commonly contain only a few tens of ppm S, whatever their fertility (Lorand, 1990). Some xenoliths from southern France, i.e. Montferrier volcano (Hérault) have very high sulfide abundances (up to 0.2 wt.%) with intergranular sulfides predominating over enclosed sulfides (Lorand and Conquéré, 1983). The process responsible for such high sulfide modal abundances and its possible effect on HSE abundances are not clear. To shed some light on this process we have carried out an extensive study of 21 xenoliths from this locality, involving major elements and lithophile trace element data, chalcogenide (S, Se) geochemistry, platinum-group element analyses and Re-Os systematics.

Montferrier xenoliths are either breccia-hosted or lava-hosted. The former have a yellowish color indicating weathering, while the lava-hosted have a fresh green color and do not show obvious alteration features. Some xenoliths display disseminated Ti-pargasite (up to 6%) regardless of their host. Montferrier peridotites are characterized by a strongly deformed porphyroclastic microstructure giving them a mylonitic appearance. It has been shown that this deformation took place at low temperature (900-750°C), probably during an uplift on the nearby Cévennes lithospheric shear zone (e.g., Fabriès et al., 1987). They also display very fertile compositions. Most of the studied samples contain between 3.0 and 4.5%  $\text{Al}_2\text{O}_3$  and the least fertile still contains 2.0 wt.%  $\text{Al}_2\text{O}_3$ .

The S concentration range (7 - 592 ppm) is the highest reported for basalt-hosted peridotite xenoliths. S contents are uncorrelated with fertility indices (e.g.,  $\text{Al}_2\text{O}_3\%$ ). Breccia-hosted xenoliths have the lowest S contents (< 100 ppm). S is negatively correlated with the percentage of sulfide alteration into hydrous iron hydroxide (up to 80%), which supports the hypothesis of weathering-related S loss (Luguet and Lorand, 1998). In contrast fresh xenoliths that are almost devoid of Fe-hydroxides have higher S contents.

Normalized trace element patterns indicate a continuous distribution between two end members (figure 1A). The first (hereafter called "depleted" pattern) displays decreasing normalized abundances from the heavy REE to the highly incompatible elements except U and Pb which show very pronounced positive anomalies (e.g.,  $\text{U}/\text{Th}_N > 10$ ). Ba and Rb enrichments are determined by amphibole. The second end-member is strongly enriched in LREE ( $\text{La}/\text{Sm}_N > 1$ ). This LREE enrichment, is accompanied by large ion lithophile elements (Sr, U, Th...), but without concomitant enrichment of the high field strength elements (Nb, Ta, Zr, Hf). In contrast to the depleted type, the U/Th ratios are chondritic. Such enriched patterns are commonly ascribed to mantle metasomatism by carbonated and/or volatile-rich small volume melts. The positive correlation of figure 1B indicates that large amounts of S have been added by this metasomatism. In thin sections, the xenoliths containing more than c.a. 200 ppm S show numerous large intergranular sulfide blebs (up to 700  $\mu\text{m}$  in maximum dimension) much richer in Fe and Cu than those from the depleted samples. Contrary to S, Se contents increase only moderately from 17-48 ppb in depleted samples to 50- 63 ppb in enriched xenoliths. The most S-rich samples may show markedly higher than chondritic S/Se ratios ( $10^4$ ) which are inconsistent with a simple addition of immiscible sulphides during metasomatism. This observation suggests that S was a dissolved species in the volatile-rich metasomatic fluid whose effects are indicated by the trace element studies.

Apart from the most refractory lherzolite which is unusually poor in PGE (total PGE = 5.2 ppb), the 8 xenoliths analyzed for the PGEs show a narrow PGE concentration range (20-28.2 ppb) independent of their fertility indices and S contents. Ru/Ir and Rh/Ir ratios are remarkably constant and slightly higher than chondritic. Pd/Ir ratios (1.37-2.26) are suprachondritic, as reported for Pyrenean orogenic lherzolites (Pattou et al., 1996) and some abyssal peridotites (Snow and Schmidt, 1998, Luguet et al., this volume). Pd/Ir ratios are correlated with S contents, mostly because the enriched samples have low Ir and Ru contents. Whole-rock fractionated Pd/Ir ratios are reflected in the pattern of the sulphides (LA-ICP-MS data). Os/Ir varies sympathetically with Pd/Ir, increasing from nearly chondritic values (1.1) in the depleted sample to suprachondritic (1.99) in the most S-

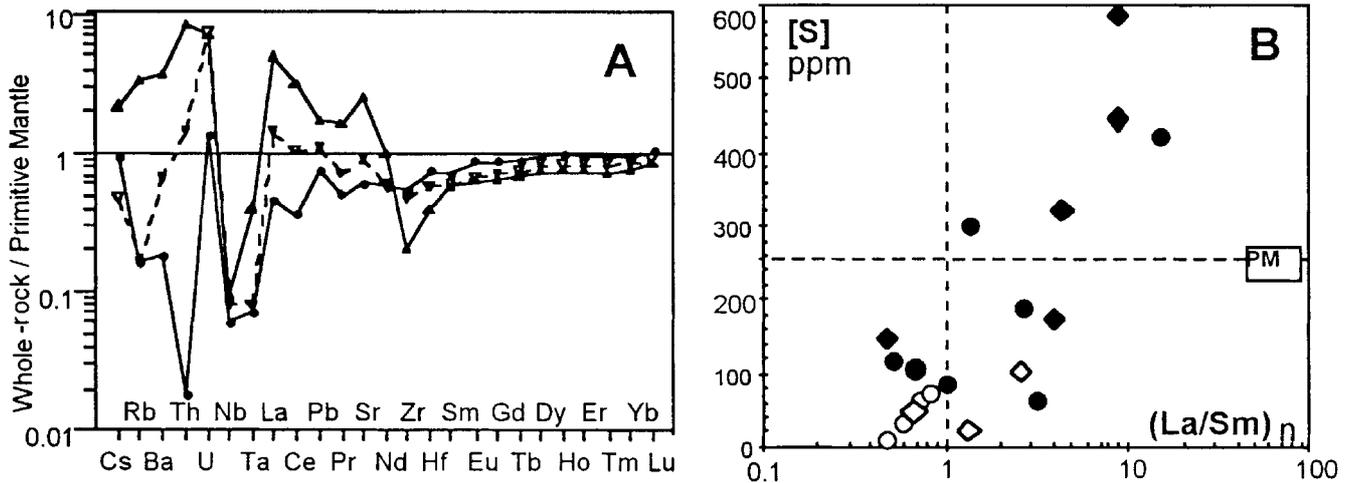


Figure 1 - A: Primitive mantle normalized trace element patterns, B: S vs.  $(La/Sm)_n$ ; black symbols are lava hosted xenoliths, white symbols represent breccia-hosted xenoliths, diamonds are for amphibole-bearing and circle for amphibole-free xenoliths. PM: Primitive mantle after McDonough and Sun (1995).

rich xenolith.  $^{187}Os/^{188}Os$  shows a similar increase from DMM-like values (0.128) in the depleted samples to highly radiogenic values (0.175) in the most S-rich sample. Our study provides further evidence that metasomatic process(es) involving volatile-rich small melt fractions may significantly alter the HSE relative abundances and Os isotopic composition of the lithospheric mantle (cf Gutierrez Narbonna et al., this volume). Such parallel variations of Os, Pd and S are consistent with the experimentally-demonstrated affinity of these elements for S-bearing vapor phases at magmatic temperatures.

## REFERENCES

- Fabries J., Figueroa O. and Lorand J.P., 1987. Petrology and thermal history of highly deformed mantle xenoliths from Montferrier, Southern France: A comparison with ultramafic complexes from the North Pyrenean Zone. *J. Petrol.*, 28: 887-919.
- Lorand J.P., 1990. Are spinel lherzolite xenoliths representative of the abundance of sulfur in the upper mantle? *Geochim. Cosmochim. Acta*, 54: 1487-1492.
- Luguet A. and Lorand J.P., 1998. Montferrier (Languedoc, France): un exemple de l'effet de l'alteration de surface sur les teneurs en soufre des xénolithes de manteau remontés par les basaltes alcalins. *C.R. Acad. Sci. Paris*, 327: 519-525.
- Pattou L., Lorand J.P. and Gros M., 1996. Non-chondritic platinum-group element ratios in the Earth's mantle. *Nature*, 379: 712-715.
- Snow J.E. and Schmidt G., 1998. Constraints on Earth accretion deduced from noble metals in the oceanic mantle. *Nature*, 391: 166-169.